



Soft X-ray absorption spectroscopic studies with different probing depths: Effect of an electrolyte additive on electrode surfaces

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HIGHLIGHTS

- We applied the soft X-ray XAS to characterize the SEI film on LIB electrodes.
- The XAS data were obtained using three detection methods with different probing depths simultaneously.
- The suppression effect of LiBOB additive on degradation of SEI was studied.

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ABSTRACT

A solid electrolyte interphase (SEI) formed on a model LiCoO₂ electrode was analyzed by the ultra-soft X-ray absorption spectroscopy (XAS). The data of Li K-, B K-, C K-, O K-, and Co L-edges spectra for the SEI film on the electrode were collected using three detection methods with different probing depths. The electrode was prepared by a pulsed laser deposition method. All the spectral data consistently indicated that the SEI film containing lithium carbonate was instantly formed just after the soak of the electrode into the electrolyte solution and that it decomposed during the repeated charge–discharge reactions. The decomposition of the SEI film seems to cause the deterioration in lithium ion battery cycle performance. By adding lithium bis(oxalate) borate (LiBOB) to the electrolyte the decomposition could be suppressed leading to longer cycle life. It was found that some of the Co ions at the electrode surface were reduced to Co(II) during the charge–discharge reactions and this reaction could also be suppressed by the addition of LiBOB.

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1. Introduction

Lithium ion battery (LIB) is a promising energy device due to its high density. While the current LIB technology is adequate for portable electronic applications, the further improvement of the battery members in terms of safety, power and cycle life is required for electric vehicle applications. It is well known that solid electrolyte interphase (SEI) film formed at the surface of the electrodes originate from the decomposition of the solvent and/or electrolyte during the initial charge process [1]. Although the SEI prevents further decomposition of electrolyte solution and improves cycle

performance, it slowly grows during charge–discharge cycles leading to increased impedance of the electrode–electrolyte interphase, and then the capacity of the battery gradually fades away. Since its chemical nature and morphology play a crucial role in the battery performance, many investigators have focused their efforts on its characterization and improvement.

The use of additives in an electrolyte is an effective approach to improving the SEI properties [2]. Lithium bis(oxalate) borate (LiBOB) has received significant attention as the additive since it forms an SEI film with superior thermal stability and better performance concerning safety [3–5]. The LiBOB additive is known to work at the negative electrode and some studies have shown that it also works at the positive electrode [6–9]. Although the SEI layers formed on the electrode surfaces in the LiBOB containing electrolyte solutions have been studied by X-ray photoelectron

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spectroscopy (XPS) and FT-IR techniques, the details still remain unclear [10–14].

X-ray absorption spectroscopy, XAS, using synchrotron radiation is sensitive to the electronic state and coordination structure of the element of interest in a sample. The spectrum of each compound has a unique feature in terms of energy position, shape and intensity of the resonances [15,16]. The XAS over the soft X-ray region (40–1000 eV) is possible to obtain the spectra of Li K-, C K-, O K-, and the first transition metal L-edges. The corresponding elements are the constituents of the SEI. B K-edge can also be an important target because the aim of this report is to find the role of the LiBOB additive in producing better SEI film.

The XAS spectra were collected for the LIB electrodes by using the total electron yield (TEY) and a fluorescence yield (FY) methods. These methods have different probing depths; ~ 10 nm for TEY, depending on the escape depth of electrons, and ~ 200 nm for FY, depending on the X-ray attenuation length in materials, respectively [17,18]. Surface sensitivity of the EY method can be increased by introducing the partial electron yield (PEY) technique (~ 2 , 3 nm), which does not detect low energy secondary electrons escaped from deeper part of the sample. When the spectral data from these three yield methods are obtained for a same sample, it is possible to analyze depth profiles non-destructively on the SEI-formed electrode surface. Since the fluorescence emission as a radiative process of atomic relaxation is of a low yield process over the soft X-ray energy region, the FY method gives us the spectra with lower signal-to-noise ratio compared to the EY method. In order to improve the quality of the FY data, we have introduced a large acceptable-area (80 mm^2) silicon drift detector (SDD) [19]. The FY spectra obtained by using the large area SDD were comparable in quality to those of EY. The detectors were arranged to the sample chamber so that all the PEY, TEY and FY data can be collected simultaneously at the same part of the sample.

The XAS spectroscopy using the above three detection modes was applied to LiCoO_2 electrode surface in the present study. The LiCoO_2 electrode used was composed of polycrystalline LiCoO_2 thin film having a flat structure in nanometer scale and similar electrochemical properties to those of composite electrodes containing graphite as an electrical conductor and polyvinylidene fluoride (PVDF) as a binder [20].

2. Experimental

LiCoO_2 thin film ca. $50 \text{ }\mu\text{m}$ in thickness was fabricated by a pulsed laser deposition (PLD) method on a flat platinum substrate. The structure and electrochemical properties are described in the previous report [20]. Its cycle performance as the cathode was evaluated by the cyclic voltammetry (CV) using a three-electrode cell with lithium metal as counter and reference electrodes. The electrolyte solutions used contained $1 \text{ mol dm}^{-3} \text{ LiClO}_4$ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 (v/v)) mixed solvent. The aim of the present experiments is to study the effect of 0.1 wt% lithium bisoxalatoborate (LiBOB) additive to the above electrolyte solutions on the formation of SEI film and thus the performance of the electrode.

Fig. 1 shows the decrease in discharge capacity after charge–discharge cycles. After 20 cycles, the electrode retained only 60% of its initial capacity. However, it could be increased to more than 90% by adding LiBOB. It is important to know the role of the additive concerning the SEI film formation.

The Li K-, B K-, C K-, O K-, and Co L-edge absorption spectra were obtained at the beam line BL-2 of Ritsumeikan University SR Center (Shiga, JAPAN). Five cathode electrodes were prepared; a pristine, a soaked in the electrolyte solution, a first charged, a first discharged, and a 20-cycled electrode. To establish the degradation mechanism

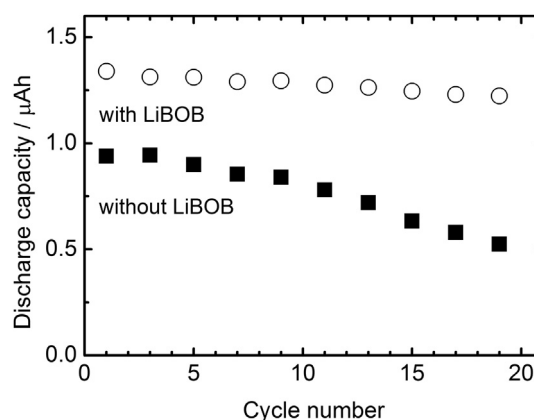


Fig. 1. Cycle performance of a $50 \text{ }\mu\text{m}$ thick LiCoO_2 electrode with and without LiBOB in the electrolyte solution. The working area of the electrode was approximately 6 mm in diameter.

during charge–discharge cycles, it is important to study the XAS spectral change carefully from the first charge and discharge processes. However, since the Li K-, C K-, O K-, and Co L-edge XAS spectra of these electrodes change very slowly with the cycle, only the results of the pristine, soaked, and 20-cycled electrodes will be given. The electrodes soaked and cycled were rinsed with dimethyl carbonate and dried in an argon filled glove box where the dew point was lower than -70°C . To avoid the exposure of the samples to the air, they were transferred to the high vacuum sample chamber of BL-2 via a transfer vessel filled with argon gas [21]. The XAS spectra were obtained in three different modes simultaneously; the partial fluorescence yield (PFY) mode with a silicon drift detector (KETEK, VITUS R100 with a $0.1 \text{ }\mu\text{m}$ Parylene-N film window), the total electron yield (TEY) mode (sample current mode), and the partial electron yield (PEY) mode (using a micro-channel plate (MCP) applying an appropriate retarding voltage in front of the MCP) [19]. In the case of Li K-edge XAS, the MCP was employed as a total fluorescent yield (TFY) detector applying high enough retarding voltage for electrons.

3. Results and discussion

Fig. 2(a) shows Co $L_{2,3}$ -edge XAS spectra obtained by the TEY method of the pristine electrode, LiCoO_2 and CoO powders as reference spectra. The peaks at 780.0 and 794.6 eV were attributed to L_3 -(pertaining to the electronic transition of $\text{Co}2p_{3/2} \rightarrow \text{O}2p\text{--Co}3d(e_g)$ hybrid states) and L_2 -($\text{Co}2p_{1/2} \rightarrow \text{O}2p\text{--Co}3d(e_g)$ hybrid states) edges. These two peaks appear at the same energies for both the pristine electrode and LiCoO_2 , indicating the covalency of 3+ for Co ions in the electrode [22].

Fig. 2(b) and (c) shows the comparisons of Co L_3 -edge spectra for the soaked and 20-cycled electrodes without and with the LiBOB additive, respectively. Small peak shift or the appearance of a lower energy component than 780 eV caused by the cycles in the surface sensitive PEY and TEY spectra in Fig. 2(b) indicates that the charge–discharge reaction causes some of the Co^{3+} ions at the electrode surface to be reduced to Co^{2+} [23]. However if the LiBOB is added, the reduction is effectively suppressed as shown in Fig. 2(c).

Fig. 3(a) shows O K-edge XAS spectra of the pristine electrode and the reference compounds, LiCoO_2 , Li_2CO_3 , and CoO collected in TEY mode. The pre-edge peak A at 529.8 eV is attributed to the transition from O 1s to $\text{O}2p\text{--Co}3d(e_g)$ hybrid states and the broadened peak over the higher energy region (higher than 535 eV) is to O 3p transitions. The spectra for the soaked and 20-cycled electrodes in the electrolyte solution without the additive are

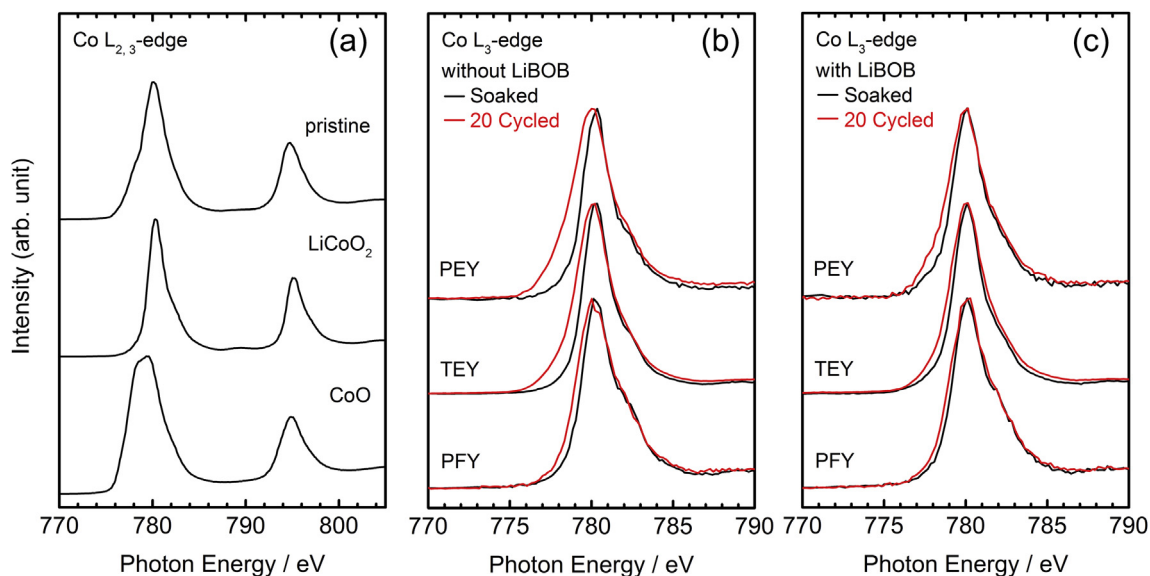


Fig. 2. Co $L_{2,3}$ -edge spectra of the pristine electrode, LiCoO_2 and CoO powders (a), of the soaked- and 20 cycled- LiCoO_2 electrode in the electrolyte solution without (b) and with 0.1 wt% LiBOB (c).

displayed in Fig. 3(b). In these spectra the peak B_1 at around 533 eV appears which can be assigned to be of lithium carbonate. This peak is most strongly observed in the PEY mode and most weakly in the PFY. This result means Li_2CO_3 is formed on the electrode surface just after the soak. In addition to the Li_2CO_3 detection by the surface sensitive PEY and TEY modes, these modes also detect the peak A at 529.8 eV assigned to bulk LiCoO_2 , indicating that the SEI layer composed of Li_2CO_3 is very thin.

By comparing the spectra in Fig. 3(b) for the soaked (black) and the 20-cycled electrode (red), it is obvious that the surface structure changes significantly after the charge–discharge reactions as indicated in the spectra obtained by the EY modes. This structure change is effectively suppressed by adding LiBOB as shown in Fig. 3(c).

Careful inspection of the PEY and TEY spectra in red in Fig. 3(b), the data obtained without the additive, indicates that after the cycles the peak B_1 of Li_2CO_3 disappears and the peak C at 531.8 eV strongly appears as a shoulder. The peak C at 531.8 eV is known to be of organic carbonyl [24]. Therefore, the charge–discharge reaction seems to remove the surface Li_2CO_3 and produce organic carbonyl compound at the surface possibly as a decomposition product of the solvent. Since the peak A of LiCoO_2 appears the most strongly even after the cycles, the carbonyl film formed at the surface must be very thin.

If the LiBOB is added to the electrolyte, the effect of charge–discharge reaction is quite different. The most surface sensitive PEY spectrum for cycled in Fig. 3(c) has strong peaks B_1 of Li_2CO_3 and C of carbonyl, and the small peak A of LiCoO_2 . The O K-edge results

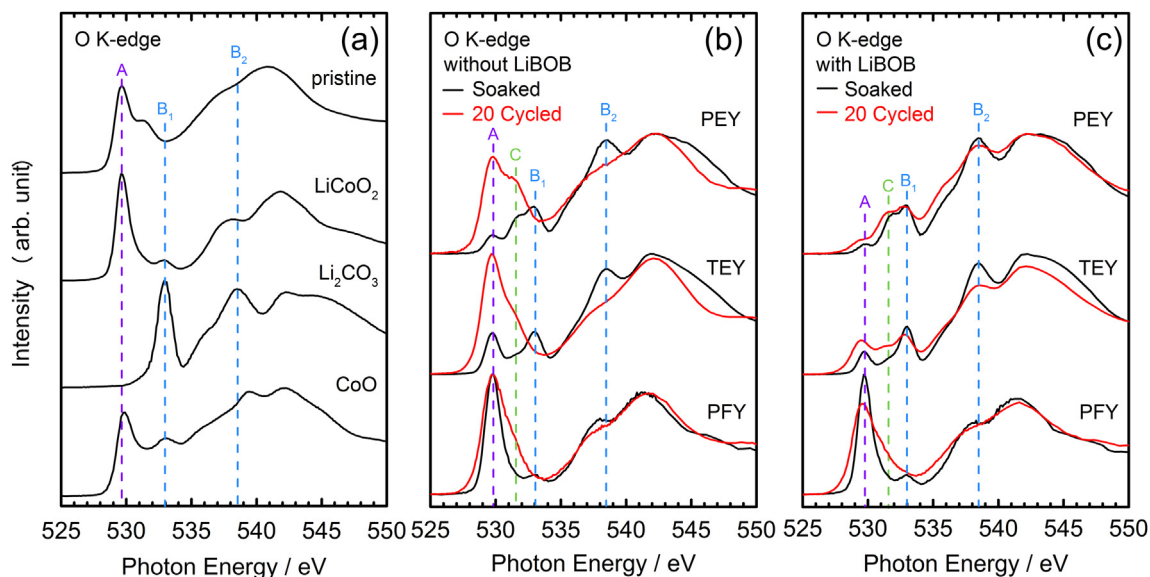


Fig. 3. O K-edge spectra of the pristine electrode, LiCoO_2 , Li_2CO_3 , CoO powders (a), the soaked- and 20 cycled- LiCoO_2 electrode in the electrolyte without (b) and with 0.1 wt% LiBOB (c).

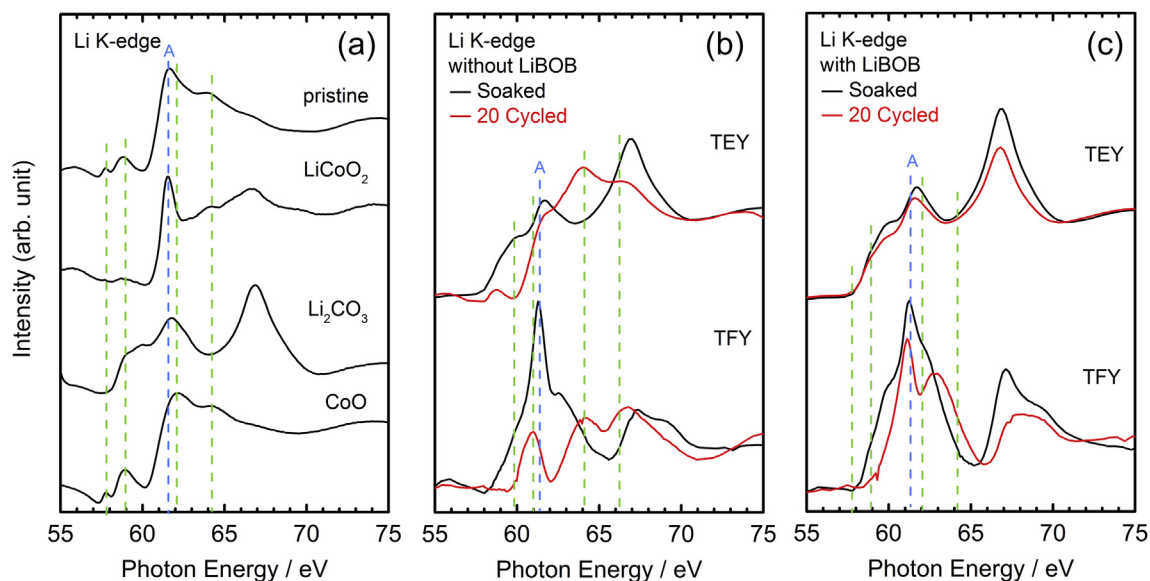


Fig. 4. Spectra over the energy region for Li K- and Co M-edges of the pristine electrode, LiCoO_2 powder, and reference samples of Li_2CO_3 and CoO (a), and the soaked- and 20-cycled- LiCoO_2 electrode in the electrolyte without (b) and with 0.1 wt% LiBOB (c).

altogether conclude that the additive protects the SEI film composed of Li_2CO_3 and carbonyl compound against the attack of the charge–discharge reaction and that without the additive the SEI film can be easily decomposed and only very thin carbonyl film remains after the reaction. Since the peaks originated from CoO appear at almost the same energies as those of LiCoO_2 , it is impossible to discuss the Co ion reduction by using O K-edge spectra.

The Li K-edge energy region spectra obtained in the TEY mode for the pristine electrode and references, LiCoO_2 , Li_2CO_3 and CoO powders, are shown in Fig. 4(a). The spectrum for LiCoO_2 has a sharp peak A at about 61.5 eV which is characteristic of ionic lithium [15,25] and the other broad peaks corresponding to Co M-edge transitions. All of these peaks are also observed in the spectrum of the pristine electrode. Fig. 4(b) and (c) shows the comparisons of the soaked and 20-cycled electrodes. The features

in the TEY spectra in black of electrodes soaked in the electrolytes both with and without LiBOB are just the same as that of Li_2CO_3 . This result is in accord with those of O K- and C K-edge, which will be discussed next, XAS data indicating Li_2CO_3 is generated on the electrode surface after the soak. Here again the addition of LiBOB protects the SEI film composed of Li_2CO_3 from the decomposition by the charge–discharge reaction as clearly indicated in the similarity of TEY spectra in Fig. 4(c). The peak A of ionic lithium at around 61.5 eV disappeared in the TEY spectra of 20-cycled electrode without LiBOB and its spectral feature there resembles that of Co M-edge for CoO indicating that the electrode surface is covered not by LiCoO_2 but cobalt compounds, possibly oxides. The formation of cobalt oxides, whose existence was also implied in the O K-edge XAS spectra, decreases the electronic or lithium ionic conductivities leading to the capacity fade [23]. The TFY spectra of the electrodes seem to contain at least two components, i.e. of Li_2CO_3

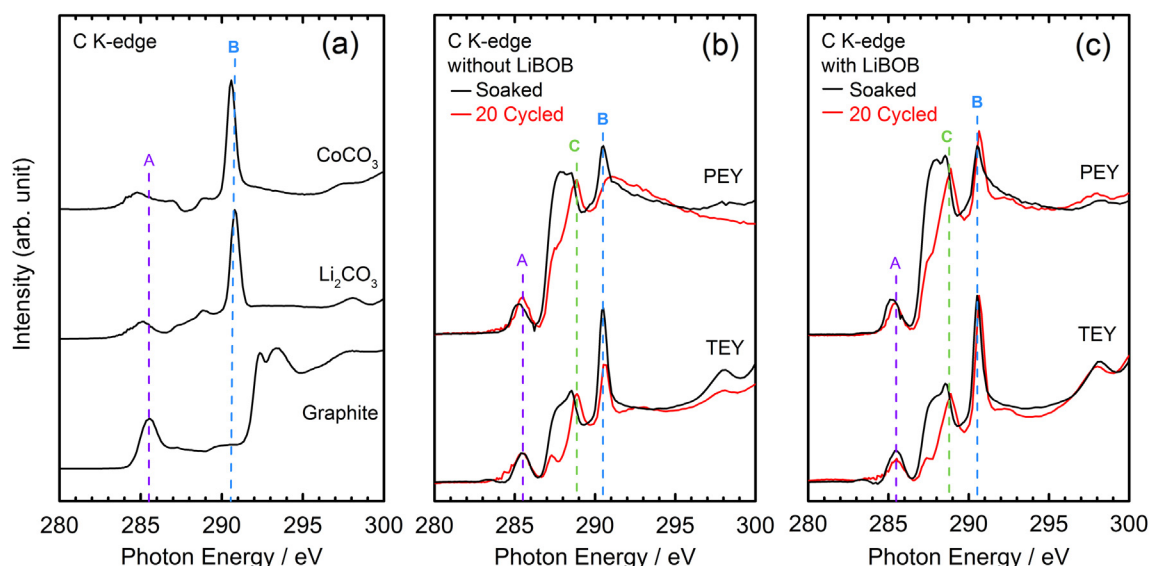


Fig. 5. C K-edge spectra of CoCO_3 , Li_2CO_3 and graphite, as references (a), soaked- and 20-cycled- LiCoO_2 electrode in the electrolyte solution without (b) and with 0.1 wt% LiBOB (c).

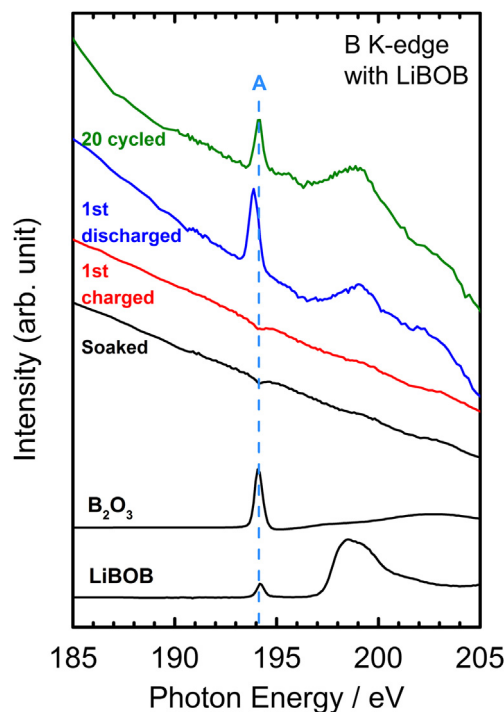


Fig. 6. B K-edge XAS spectra (TEY) of LiCoO₂ electrode soaked, first-charged, first-discharged and cycled in an electrolyte solution containing 0.1 wt% LiBOB.

and LiCoO₂. Since the TFY mode over the Li K-edge energy region is relatively surface sensitive because of large X-ray photon absorbance for material at this low energy region, its spectral feature is the mixture of those for both the bulk LiCoO₂ and the SEI film containing Li₂CO₃.

Fig. 5(a) shows C K-edge XAS spectra of CoCO₃, Li₂CO₃ and graphite as references collected in TEY mode. The peak A at 285.5 eV is attributed to a double bond carbon (C=C) and peak B at 290.8 eV is to carbonate (CO₃²⁻). The comparison of TEY and PEY spectra of the soaked and 20-cycled electrode in the electrolyte solutions without and with LiBOB are shown in Fig. 5(b) and (c), respectively. All the soaked spectra show the peak B of carbonate (290.8 eV), the peak C of C–H (289 eV) and the peak A of C=C (285.5 eV) regardless of the LiBOB addition, implying the decomposition of electrolyte solution at the electrode surface and the generation of carbonates and alkyl compounds [26]. The peak C assigned to alkyl compounds does not change much with cycles.

The behavior of peak B in Fig. 5(b) indicates that the carbonyl (from solvent) or carbonate (of lithium salt) present at the surface of soaked electrode almost disappears at the surface (PEY result) after the charge–discharge reactions. While the results given in Fig. 5(c) show that the LiBOB additive prevents the surface composition change by the reactions, so the surface is covered by Li₂CO₃ SEI securely.

Fig. 6 shows B K-edge TEY spectra of the electrodes treated in the solution containing LiBOB and reference materials, a four-coordinated boron oxide (B₂O₃) and LiBOB. The peak at 194 eV, corresponding to a four coordinated boron compound [27], did not appear in the spectra of the soaked and first-charged electrode but appeared after the first-discharge. Since the spectral feature of the electrodes is not of the LiBOB nor B₂O₃, the four-coordinated boron compound found on the surface might be assigned to the decomposition product of BOB⁻ anion left at the surface when the Li⁺ ions were inserted into the LiCoO₂ cathode during the discharge process, while the reports by NMR study [12] and by XPS [14]

suggested the formation of three-coordinated boron compound during the charge–discharge cycle. After twenty-cycles, the sharp peak around 194 eV shifted slightly, indicating further reaction of the four-coordinated product at the surface during charge–discharge cycles. Although the details of the reactions and products are not clear, we believe that the four-coordinated boron product formed during the first discharge protected the SEI layer from its decompositions.

4. Conclusions

The effect of LiBOB addition to the electrolyte on the character of the SEI layer formed on a LiCoO₂ thin film electrode was investigated using soft X-ray XAS analysis. PEY, TEY and FY methods were used to collect the spectra simultaneously. These methods have different probing depths. At the surface of the electrode Co ion was found to be reduced to Co²⁺ after 20 cycles of charge–discharge reactions and by adding the LiBOB the reduction was suppressed. The SEI layer was found to contain Li₂CO₃ which seemed to play an important role for the LIB cyclability. If the additive of LiBOB was not present, the SEI containing Li₂CO₃ decomposed after the charge–discharge reactions but its addition prevented from the decomposition. B K-edge XAS spectra for first-discharged and 20-cycled electrodes showed a sharp peak characteristic of the four-coordinated boron compound indicating its formation in the SEI layer. This boron species seems to protect the SEI layer from degradation during the charge–discharge cycles resulting in longer cycle life.

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